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### **Apatite forming ability of bivalve (Meretrix)-peek composite material**

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#### **ABSTRACT**

*A neoteric modus operandi to trigger the growth of Hydroxyapatite (HAp) composite from Bivalve (Meretrix) is systemized for bone healing. The methodology is effectuated by compaction and pressure less sintering at an intense temperature. Hydroxyapatite (HAp) supplemented with carbonate is the resultant product to the exclusion of everything else in the aforesaid reaction. The end product is set apart by Energy Dispersive Spectrum and Scanning Electron Microscopy (SEM).*

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#### **INTRODUCTION**

Historically, a wide variety of materials have been used as bone / tooth replacement, including animal teeth, human teeth, sea shells, ivory, bone, hydroxy apatite, cobalt-chromium alloy and titanium, although the later three materials have not been used for tooth implants until the past several decades. Materials for the bone replacements have evolved more slowly over the past several centuries. The possible four materials group used includes metals, ceramics, composites and polymers. In spite of recent improvements with physical properties of these materials none of these are permanent. Material scientists will continue searching into the twenty-first century for the restorative materials that bond permanently to the body. Hence it is essential to find out suitable biocompatible materials.

Among the bioactive materials, polymers have attracted much attention. Hence it would be helpful to the society to identify the bioactive polymers through their apatite forming ability. In

recent years, the emphasis on the development of biomaterials has shifted from monoliths to composites [1,2]. By controlling the volume fraction and distribution of the second phase in the composite, the properties of composites can be controlled to meet mechanical and physiological requirements as an implant. In this respect, hydroxyapatite (HA)-reinforced high-density polyethylene (HDPE) composites (HAPEXTM) [3] have been developed successfully for clinical application. Following this concept of incorporating the bioactive ceramics into biocompatible polymer to increase stiffness and bioactivity, various bioactive ceramics, such as bioglass, HA and tricalcium phosphate (TCP) in biocompatible polymer matrix-like polysulfone (PS) and polyhydroxybutyrate (PHB) have been developed to produce bone substitutes [4–6]. Among them, synthetic HA, which is similar to the main mineral phase of the bone, has been widely used as a bone substitute material due to its biocompatibility and bone bonding ability [7]. Polyetheretherketone (PEEK) is a rigid semi-crystalline polymer with excellent mechanical properties and high resistance to various chemicals and radiations. Recently, much attention has been given to PEEK Polymer composite for load-bearing orthopedic applications [8-12]. Researchers have developed Glass fiber (GF)/PEEK [9] and carbon fiber (CF) PEEK [10] composites to produce hip joint prosthesis and the reported Young's modulus of the latter reached up to 14GPa at 30 vol% carbon. The Young's modulus and the tensile strength of injection molded HA/PEEK composite were reported to be in the range of 3–10GPa and 40–90MPa, respectively [11,12]. These results indicate that the mechanical properties of HA/ PEEK composites are in the regime of cortical bone, making these composites a potential candidate for use in load-bearing applications. Although the mechanical properties of these composites have been well documented, the bioactivity of these composites is not studied in detail.

Bone / teeth repair is a subject of intensive investigation of human health care. More and more often, medical devices or prostheses are implanted in the human body. These materials need to be accepted by the tissues in which they are placed in addition to performing their intended function over lifetime. In bony tissue, it is required that the implants are stable for a long period and firmly fixed to bone.

All the bioactive materials form an apatite layer on their surfaces in the living body and bond to living bone through the apatite layer or its components such as CaO and P<sub>2</sub>O<sub>5</sub>. Therefore, it has been assumed that the essential requirement for an artificial material to bond to living bone is the presence of the apatite or its components in it. This apatite layer can be reproduced on the surfaces of all the bioactive materials even in a cellular simulated body fluid with ion concentration nearly equal to those of human body plasma. Bone-producing cell, called osteoblast, can preferentially proliferate and differentiate on this bone like apatite layer whose characters are very similar to those of the apatite in the bone. Consequently, the surrounding bone can come into direct contact with the surface apatite layer of the bioactive materials without forming the fibrous tissues around them [13]. When this occurs, a tight chemical bond is formed between the surface apatite and the bone apatite. It can be concluded that the essential requirements for an artificial material to bond to living bone is the formation of biologically active bone like apatite layer on its surface in the living body.

However, the *in vivo* results are normally difficult to obtain and, subsequently, to interpret due to lack of animal source and the complexity of cellular responses. Previous studies [14] have shown

that formation of biological apatite on the surface of artificial bioactive materials is critical to establishing bonding between living tissue and biomaterials.

This project is aimed to synthesis and use optical techniques to identify apatite forming composite biomaterial. It was reported that Bivalve (Meretrix) contain calcium carbonate. The plan of the present work is, therefore, to investigate the growth of apatite layer on Bivalve (Meretrix) /PEEK instead of HA/PEEK [11,12] composites with 80 wt% fractions up on immersing in SBF.

### EXPERIMENTAL SECTION

Polyetheretherketone (PEEK) is a rigid semi-crystalline polymer with excellent mechanical properties and high resistance to various chemicals and radiations. Much attention has been given to PEEK Polymer composite for load-bearing orthopedic applications [8-12]. It was reported that the Young's modulus and the tensile strength of HA/PEEK composite to be in the range of 3–10GPa and 40–90MPa, respectively [11,12]. The marine based drugs are usually rich in calcium. The Bivalve (Meretrix) and PEEK powders were mixed at the desired weight percentage of (80 wt%) of Bivalve (Meretrix) and blended for 3 hrs to obtain a homogeneous powder mixture. The mixed powders were die-pressed into disks of 10 mm diameter with 3mm height. The compacts were then sintered at 365 °C for 30 min in an atmospheric furnace. Figure 1 shows the Bivalve (Meretrix) and PEEK- Bivalve (Meretrix) Pellet.



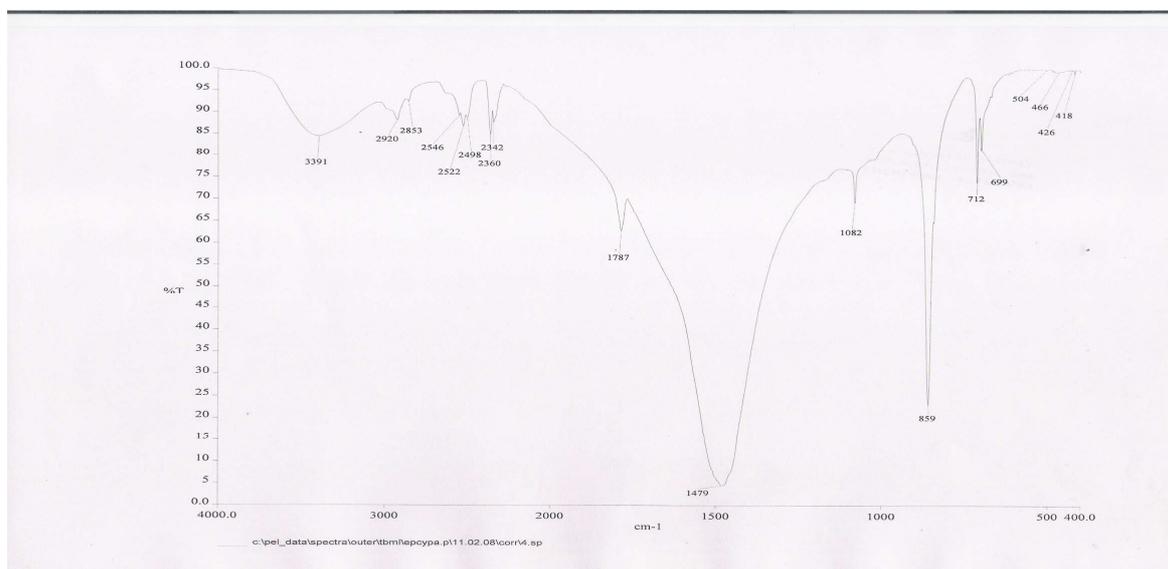
Figure 1: Bivalve (Meretrix) and PEEK- Bivalve (Meretrix) Pellet

FTIR spectra of the raw sample (Bivalve), sample heated in Atomic Furnace is shown the following Figure 2. In the sample the Carbonate ions in the mineral were demonstrated by the internal vibration modes of the  $\text{CO}_3^{2-}$  ions, 713, 700 ( $\nu_4$ ) – 864, 844 ( $\nu_2$ )- 1090 ( $\nu_1$ ) and 1490 ( $\nu_3$ )  $\text{cm}^{-1}$ . The strong band detected at 1792  $\text{cm}^{-1}$  could also be attributed to the C=O groups of the carbonate ions. The splitting of ( $\nu_4$ ) is characteristic of aragonite structure.

#### Immersion of HA/PEEK composite in simulated body fluid

The SBF was prepared by dissolving the reagent grade NaCl,  $\text{NaHCO}_3$ , KCl,  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  into distilled water, and buffered with Tris (hydroxymethyl-aminomethane,  $\text{NH}_2\text{C}(\text{CH}_2\text{OH})_3$ ) and hydrochloric acid (HCl) to pH 7.4 at 37 °C [15]. The concentration of different ionic species in SBF closely resembles with that of human blood plasma, as listed in Table 1. Specimen was immersed in 50 ml of SBF for 7days at 37 °C. The

temperature was maintained using a water bath. Upon removal from SBF, the specimens were gently rinsed with distilled water and dried overnight at 60°C.



**Figure 2.** FTIR spectra of the raw sample (Bivalve) heated in Atomic Furnace.

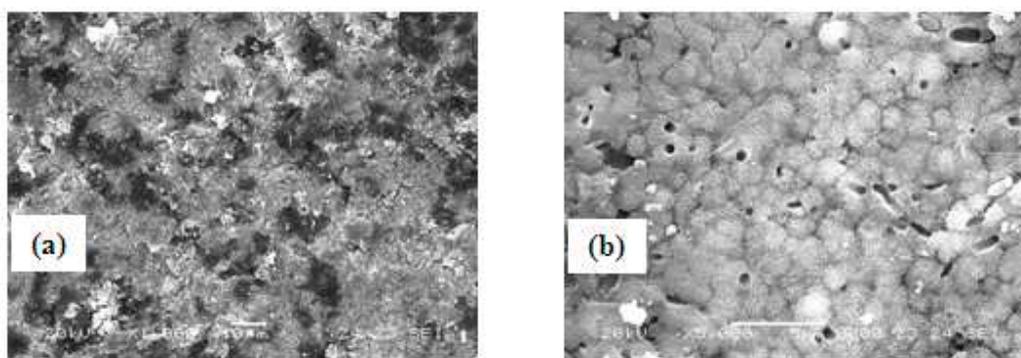
**Table –1** Ion concentration of SBF in comparison with human blood plasma

Ion Species	Ion Concentration (mmol <sup>l</sup> <sup>-1</sup> )	
	SBF Solution	Human blood plasma
Ca <sup>2+</sup>	2.5	2.5
Na <sup>+</sup>	142.0	142.0
K <sup>+</sup>	5.0	5.0
Mg <sup>2+</sup>	1.5	1.5
Cl <sup>-</sup>	147.8	103.0
HCO <sub>3</sub> <sup>-</sup>	4.2	27
HPO <sub>4</sub> <sup>2-</sup>	1.0	1.0
SO <sub>4</sub> <sup>-</sup>	0.5	0.5

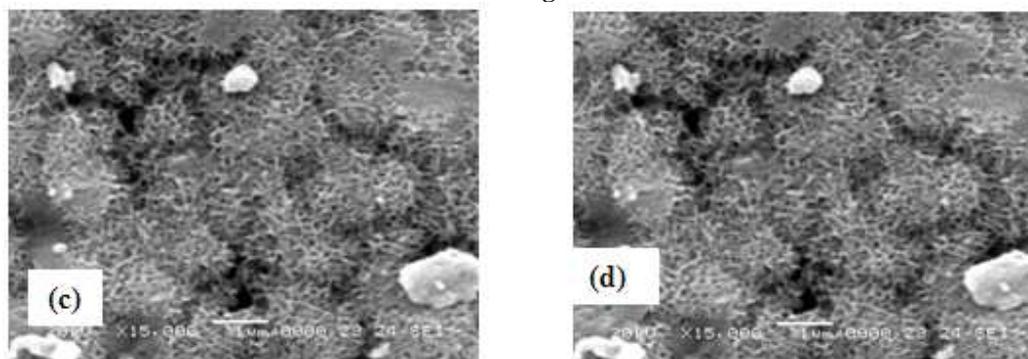
### SEM analysis of PEEK/ Bivalve (Meretrix)

A JEOL JSM 5610 SEM was used throughout for the morphology studies of the samples. Figure 3 and Figure 4 shows the surface morphology of composite materials. Figure 3 (a) shows the surface morphology of pure PEEK/ Bivalve (Meretrix) compacts before immersion in SBF. The pure PEEK is an inert material in SBF and it does not induce HCA formation [16]. Figures 3 (b),

(c) and (d) shows the surface morphology of the as-prepared Bivalve (Meretrix) PEEK composites, after 7 days of immersion in SBF with different magnifications, where it can be seen that the HA particles (bright) were evenly distributed in PEEK matrix. It is evident that small spherical crystals appeared on the surface of the composites Bivalve (Meretrix) /PEEK composites. In this view, the crystals precipitated from the SBF can be seen clearly, which appears as a continuous layer from composite disk. In 1000 magnification bizarre shallow dip patterns appear in this composite materials. At higher magnification, this layer appeared to be consisting of many nano-sized flaky crystallites with a dune-like morphology (Figure 3.d), as observed by others in similar systems [17-19]. From the Figure 4 ie the Energy Dispersive Spectrum of the immersed sample it reveals that the formed apatite is calcium rich apatite. Normal bone has Ca/P ratio as 1.67 whereas in this case the Ca/P is 2.49.

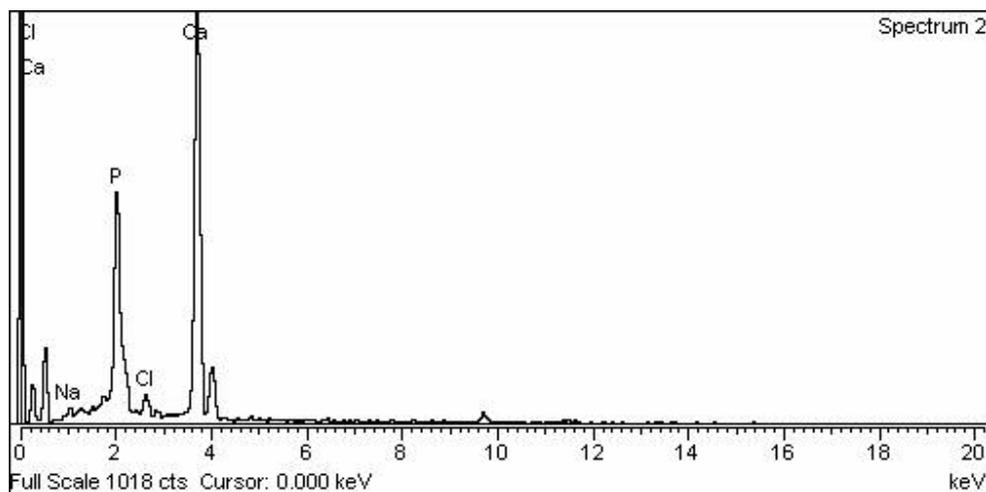


**Figure 3: SEM Image of PEEK/ Bivalve (Meretrix) Surface (a) Before (b) After 7 days immersion in SBF with 1000 magnification**



**Figure 3: SEM image of the surface of PEEK/ Bivalve (Meretrix) composites immersed in SBF (c) 15000 magnification (d) 25000 magnification**

Element	Weight%	Atomic%
Na K	2.16	3.46
P K	22.31	26.57
Cl K	3.50	3.64
Ca K	72.04	66.32
Totals	100.00	



**Figure 4:** EDS image of the surface of PEEK/ Bivalve (Meretrix) composites immersed in SBF .

### CONCLUSION

- The SBF has also proven to be useful in predicting the bone-bonding ability of materials.
- Composite material containing calcium carbonate is capable of enhancing the bond formation to bone.
- Composite treated in Atmospheric Furnace is capable of producing apatite.
- Appearance of apatite layer on the composite material in the presence of SBF shows clearly this composite can be used as bone repairing biomaterial.
- At higher magnification, nano-sized flaky crystallites with a dune-like morphology appearance can be considered as a confirmatory test for apatite.

### Suggestions

- Apatite layer presence in all the Bivalve (Meretrix) can be confirmed by FTIR and XRD studies and apatite formation could be optimized by varying the Bivalve (Meretrix) wt% in the composite.
- FTIR and XRD study throw light on identification of type of apatite and its structure.
- Growth Kinetics of apatite formation can also be studied and the true importance of this treatment, however, is that it can be easily applied for all apatite-forming materials in SBF.
- Mechanical property of pure PEEK material is known, it would be very much useful if a study on mechanical property of the composite material is carried out.
- A thorough study should be employed in Bivalve (Meretrix) /PEEK composite for better understanding of chemical changes.

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